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SCIENCE

A WEEKLY JOURNAL DEVOTED TO THE ADVANCEMENT OF SCIENCE, PUBLISHING THE
OFFICIAL NOTICES AND PROCEEDINGS OF THE AMERICAN ASSOCIATION
FOR THE ADVANCEMENT OF SCIENCE

FRIDAY, NOVEMBER 1, 1907

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THE VAGARIES OF BERYLLIUM¹

As it has become a custom in the Ameri- can Chemical Society that the chairmen of the various sections, into which the sessions of the general meetings are divided, shall present an address upon some branch of their work in which they are especially in- terested, I have decided to speak this morn- ing upon beryllium and especially upon those peculiarities of the element which stand out prominently as characteristic of itself. I realize fully the narrowness of the subject and fear that what I have to say will scarcely be of interest to all of you, but must plead as my excuse that, realizing fully the limitations of my own knowledge, I can select no other subject with which I am more familiar.

Even at its christening beryllium started on a vagarious career and its early sponsors as well as those who followed have recognized it under different names and have ascribed to it and to its compounds properties as widely variant as the condi- tions under which they worked. Referred to first by Vauquelin, its discoverer, as "la terre du Béril" the German translators naturally adopted Berylerde as the name of its oxide and although Vauquelin later ac- cepted, under virtual protest, the sugges- tion made that glucine be used on account of the sweetish taste of the salts of the element, the name never secured adoption

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¹ Address of the chairman of the Section on Inorganic Chemistry, Toronto Meeting, American Chemical Society.

outside of France and in the early literature was frequently written glycine. When later the element itself was separated by Wohler he used the term beryllium for the first time and a few weeks after glucinium appeared in the French press due to Bussy's almost simultaneous discovery. It is useless to go into the subsequent usage of the term or why the "i" was dropped and glucinum used for a time in American practise. It is sufficient, I think, to say that by far the majority of chemists of the world prefer and use the name beryllium in their conversation and writings, and since neither priority nor usage can be shown for glucinium it should be dropped as rapidly as possible in the interests of uniformity. I especially believe this to be true since there is no prospect of its ever replacing the more popular and, in my opinion, more justifiable beryllium.

Although the literature of inorganic chemistry is quite generally overburdened with compounds which have no actual existence and which have obtained place and been assigned formulas simply by the *analysis* of solid phases obtained under variable conditions and without other attempt to prove their individuality, it is doubtful if there is any branch of the field that needs more careful revision than the chemistry of beryllium. Its literature is full of errors. Compound after compound has been claimed which has no actual individual existence, but whose place in literature and whose formula depend solely upon analysis of mixed crystals, residues of evaporation or indefinite gummy precipitates, without attempt to separate the individuals present. Formerly this could not always be done, but with the more recent and simple applications of the phase rule to these problems there is no excuse for similar errors which, unfortunately, still continue to creep into our journals.

The metal beryllium itself has been but

little studied, and for the main part simply as a dark steel-gray powder obtained by the reduction of its chloride by sodium or potassium or as small hexagonal plates obtained by the electrolysis of its double fluorides in a manner quite similar to the production of aluminum. Its melting point, its solution tension and many others of its important properties have never been determined, and many diverse statements are to be found in regard to it, although the very careful researches of Lebeau can undoubtedly be fully relied upon so far as he went into the subject. It is recorded, for example, that it does and it does not combine directly with hydrogen, sulphur, selenium and phosphorus, that it is and it is not reduced from its oxide by aluminum and magnesium, that it has been produced (even manufactured) by the electrolysis of its bromide and that its bromide is not a conductor of electricity. In each case the negative is probably true. For many years its valency was, and, for that matter, still is a matter of dispute. Even before it was seen that the only vacant place for beryllium in the periodic system was between lithium and boron, there were strong arguments for both its divalency and its trivalency on account of its close resemblance to both zinc and aluminum in its action. When Mendeléef finally pointed out its proper place in his table the controversy grew even more animated and most of the researches on the element in the seventies and eighties had the establishment of the true valency as the main object. All the early determinations of the specific heat lead to the figure 13.6 as the atomic weight and it was not until Nilson and Pettersson, after conquering unusual difficulties in a masterly research, finally determined the vapor density of the chloride and established its formula as BeCl_2 that real light was thrown on the problem. Shortly afterward in 1886 Humpidge showed that beryllium was abnormal as to its specific

heat, which increased regularly with the temperature at which determined, until between 400° and 500° it approached normal with a value of 6.2. A determination of the vapor density of the bromide, of the acetylacetonate and of the basic acetate, all seemingly in agreement with the idea of the divalency of the element, would have seemed to have settled the matter and probably has done so, but the controversy itself goes merrily on. Wyruboff still argues in his articles for the trivalency and Tanatar claims that the basic acetate can only be explained on the supposition that the element is in reality tetravalent.

Of the binary compounds of beryllium only the oxide, the carbids and the halides have any real standing in literature, although the sulphide has been made by Lebeau. Of these the oxide is the only one that is stable in ordinary moist air and even it shows decided variability in its hydropiscopy for reasons not yet determined. Ordinarily white, it is said to be blue by Levi-Malvano when made from his hexahydrated sulphate, although it is almost inconceivable that the difference of two molecules of water in the sulphate should cause this change and the existence of the hexahydrate itself is not yet confirmed. The halides, with the possible exception of the fluoride, can only exist in the complete absence of water, which causes them immediately and violently to lose part of their anion as hydracid. In this respect they are even more sensitive than the corresponding compounds of aluminum. On evaporating their solutions in water they lose more or less of the remainder of the gaseous hydracids, the residue becoming more and more basic and remaining soluble until a surprising degree of basicity is reached. This hydrolytic action is comparatively small in the case of the fluoride, but is practically complete in the case of the chloride, bromide and iodide. By care-

ful manipulation residues of almost any degree of basicity, up to the pure oxide, can be obtained, and these mixtures of base and normal salt have given rise to claims for numerous *oxyfluorides* and oxychlorides for the existence of which there is no other evidence than the analysis of the variable residues obtained.

The hydroxide of beryllium is one of the most interesting of its compounds and one that has properties which vary greatly with the conditions of its preparation. Among the most noteworthy may well be mentioned its great solubility, of from two to five equivalents, in concentrated solutions of its own salts, and its precipitation therefrom on dilution; its solubility in saturated solutions of acid sodium and ammonium carbonates, and its very much diminished susceptibility to reagents when dried at high temperature or boiled in water, as instanced by the fact that when freshly precipitated and washed with cold water it will take up one third of an equivalent of carbon dioxide, but on boiling becomes so immune to its action that the gas has been passed through it for three months without any considerable absorption.

Probably the fact which has the greatest bearing upon the chemistry of beryllium and has caused more failures of researches undertaken upon the element than any other one thing, is the great influence which water has upon all of its salts, acting to many of them almost as if it were itself a strong hydroxide and in a manner that is hard to understand from our ordinary conceptions of solution and hydrolysis.

For this reason normal salts of the non-volatile acids only can be crystallized from water, and indeed but very few of them, such as the sulphate, the selenate and the oxalate have been so prepared. These are so strongly acid in reaction that they act almost as solutions of the acids themselves, attacking metals with evolution of hydro-

gen, setting free carbon dioxide from carbonates and reddening litmus even after surprising quantities of free base have been added. In spite of this fact the sulphate, chloride and nitrate have been shown to be less hydrolyzed, as determined by the sugar inversion method, than the corresponding salts of aluminum and iron, although they attack metals and carbonates vigorously even after many times enough excess of their own hydroxide has been dissolved to throw back the hydrolysis. Other normal salts like the nitrate can be prepared only by crystallizing from concentrated acid, and even anhydrous acid yields only basic compounds in the case of the fatty acid series. Normal salts of more readily volatile acids, like the nitrite and carbonate, have not been produced at all or only, as in the case of the sulphite, from absolute alcohol or, as with the halides, by the direct combination of the elements themselves, with special precautions to eliminate water. Many normal salts, such as the borates, the chlorates, the bromates, the iodates, the chromates, the acetates, etc., have not been obtained, apparently because a concentration of acid sufficient to overcome the so-called hydrolytic solution tension of the salts can not be attained.

On the other hand, only one *acid* salt, the mono acid phosphate, has any real claim for recognition and, although the peculiar nature of phosphoric acid would seem to render the existence of this compound as probable as any of an acid nature, its existence rests solely upon the testimony of a single analysis of a non-crystalline precipitate obtained by Scheffer nearly fifty years ago.

The action of water upon the compounds of beryllium is highly modified, as is the case with some of the compounds of aluminum and magnesium, by the entrance of another metallic element into the molecule, and some of the double salts of this element

are well defined and readily obtained in the presence of water, where the simple normal salt could not be produced at all or only with difficulty. This is notably true of the double carbonates, chlorides, iodides, nitrites and sulphites, although in general these salts have been studied but little, their discoverers being content with their identification and analysis. Among the double salts time permits of the mention only of the truly interesting double alkali tartrates and malates studied by Rosenheim and Itsig, and of the remarkable fact that the introduction of beryllium into their molecule enormously increases the molecular rotation of the compound, so that the diberyllium alkali tartrates have from five to six times the molecular rotation of the corresponding alkali bitartrates, and the diberyllium malates a molecular rotation more than twenty times as great as the alkali bimalates. This is particularly surprising since Walden has shown that beryllium has no undue influence upon the molecular rotation of the alpha brom camphor sulphonates.

Some of the most interesting problems of the chemistry of beryllium lie in the equilibrium relations that exist between the various acid radicals and quantities of the oxide in excess of that required to produce the normal salt, *i. e.*, in the so-called basic compounds. It is certainly true that many of these acids can hold in solution phenomenally large amounts of beryllium oxide or hydroxide, extending in the case of the acetate to six equivalents, while the chloride can hold four, the sulphate three and the oxalate nearly three equivalents. Even after these abnormal amounts have been dissolved the solutions still remain acid to litmus, and if heated in contact with basic beryllium carbonate the carbonate is attacked, the carbon dioxide set free and an equivalent amount of hydroxide thrown out of solution. These highly concentrated

solutions, on being diluted with water, throw down precipitates of a highly basic nature, or on evaporation leave gummy masses, the basicity of which depends upon the amount of the dissolved hydroxide, while, physically, they differ but little. Both the precipitated bodies and the residues of evaporation are amorphous and glassy in structure and vary widely in composition. The basic precipitates on equilibrium, being reached, approach closely to the hydroxide in composition, but always contain a small amount of occluded acid or normal salt, which it is impossible to entirely remove by washing. These facts have given rise in literature to a large number of so-called basic compounds which have no existence as independent individuals, but are in reality the impure hydroxide, or, perhaps, more properly come under the domain of homogeneous phases of variable composition or solid solutions.

It is, indeed, difficult to understand how the solution of the normal sulphate, nitrate and chloride can dissolve several equivalents of their own hydroxide, attack metals and carbonates almost as vigorously as if they were the free acids themselves yielding these basic solutions, and still be less hydrolized than the corresponding salts of aluminum and iron as Leys and Brunner have both shown to be the case. It is, perhaps, equally difficult to demonstrate why the basic solutions so obtained should have less osmotic activity per equivalent of the acid present than the normal salts, should show no indication of a colloidal nature and should contain no complex anion, but this is, indeed, the fact. The most probable explanation would seem to be that we have here a case of simple solution of a substance (beryllium hydroxide) in a mixed solvent (water and normal salt) in one of which alone (water) it is insoluble. The whole action of these solutions is perfectly analogous to those cases where a

substance, being dissolved in a mixed solvent, *raises* the freezing point whenever it is insoluble in that component which separates as the solid phase on cooling and which Miller has mathematically shown is a necessary sequence of the theorem of Gibbs.

In contradistinction to the basic solutions, solid or liquid, already mentioned, we have the truly phenomenal and actually basic compounds of beryllium, discovered in Urbain's laboratory by Lacombe, which are produced pure only in contact with anhydrous acid or acid so nearly anhydrous that the mass of the water present becomes negligible to produce hydrolysis. These very interesting, volatile and perfectly unique basic compounds are apparently confined to the fatty acid series and have the general formula $\text{Be}_4\text{O}(\text{AC})_6$. Of these the formate, acetate, propionate, butyrate, isobutyrate and isovalerianate have been made and studied.

And now after this brief summary of the main characteristics of the chief classes of beryllium compounds I must, in closing, honor those who have been most prominent in developing our knowledge of this element by mentioning the names of Vauquelin, Wöhler, Bussy, Andejew, Weeren, Debray, Joy, Gibbs, Atterberg, Nilson and Pettersson, Humpidge, Hartly, Krüss and Moraht, Lebeau, Rosenheim and Itsig, and Urbain and Lacombe and paying my sincere respect to the many others who, from time to time, have struggled through the difficulties incident to the peculiar and decidedly vagarious action of this element to greater light and truth. And finally I feel that I should call the attention of this inorganic section most particularly to the fact that not only the future chemistry of beryllium, but of all the elements in our branch of the greatest of sciences, is becoming more and more dependent for its exactness and wealth of discovery upon the

application of those laws which are now correlated under the head of physical chemistry. At the same time we must not be engulfed by this more recent branch of our science, but must always look to her as the handmaiden and not the mistress.

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*THE APPLICATION OF SCIENTIFIC METHOD
TO EDUCATIONAL PROBLEMS*¹

NOTWITHSTANDING the fact that the greater part of my life has been spent in educational work, in teaching, in examining, in organization, and in the investigation of foreign systems of instruction, I have experienced considerable difficulty in selecting, from the large number of subjects that crowd upon me, a suitable one on which to address you as president of a section of the British Association devoted to educational science.

At the outset I am troubled by the title of the section over which I have the honor to preside. I can not refrain from asking myself the question, Is there an educational science, and if so, what is its scope and on what foundations does it rest? The object of the British Association is the advancement of science, and year by year new facts are recorded in different branches of inquiry, on which fresh conclusions can be based. The progress of past years, whether in chemistry, physics or biology, can be stated. Can the same be said, and in the same sense, of education? It is true that the area of educational influence is being constantly extended. Schools of every type and grade are multiplied, but is there any corresponding advance in our knowledge of the principles that should govern and determine our educational efforts, or which can justify us in describing such

knowledge as science? If we take science to mean, as commonly understood, organized knowledge, and if we are to test the claim of any body of facts and principles to be regarded as science by the ability to predict, which the knowledge of those facts and principles confers, can we say that there exists an organized and orderly arrangement of educational truths, or that we can logically, by any causative sequence, connect training and character either in the individual or in the nation? Can we indicate, with any approach to certainty, the effects on either the one or the other of any particular scheme of education which may be provided? It is very doubtful whether we can say that educational science is yet sufficiently advanced to satisfy these tests.

But although education may not yet fulfil all the conditions which justify its claim to be regarded as a science, we are able to affirm that the methods of science, applicable to investigations in other branches of knowledge, are equally applicable to the elucidation of educational problems. To have reached this position is to have made some progress. For we now see that if we are ever to succeed in arriving at fixed principles for guidance in determining the many difficult and intricate questions which arise in connection with the provision of a national system of education, or the solution of educational problems, we must proceed by the same methods of logical inquiry as we should adopt in investigating any other subject matter.

In order to bring education within the range of subjects which should occupy a place in the work of this association, our first efforts should be directed towards obtaining a sufficient body of information from all available sources, past and present, to afford data for the comparisons on which our conclusions may be based. One

¹Address of the president of the Educational Science Section of the British Association for the Advancement of Science, Leicester, 1907.